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AN EVALUATION OF HACH DIRECT READING
ENGINEER'S LABORATORY

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Federal Water Pollution Control Administration
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Division of Technical Services

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
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INTRODUCTION

The proper selection of sampling sites is of primary importance to the evaluation of water quality of a designated water body. When background data are not available on a given water body, sampling site selection may be limited to visual observations and known waste outfalls. If a rapid, accurate and convenient method to determine water quality prior to intensive study were available, sampling site selection would be simplified.

Hach Chemical Company has designed a portable "Hach Direct Reading Engineer's Laboratory"* that could be used for this purpose. The practicality of this kit for field reconnaissance work was determined.

DESCRIPTION

The "Hach Direct Reading Engineer's Laboratory" (Model DR-EL) is a compact, rugged field kit. The case is molded plastic, 24 X 8 X 10 inches with a total weight of 31 pounds when full of necessary equipment. The kit contains a colorimeter and a sturdy burette

*Mention of a commercial product does not constitute endorsement by the Federal Water Pollution Control Administration, Department of the Interior.

assembly for volumetric tests. The reagents are either in the form of "powder pillows," which are preweighed reagents in sealed non-breakable containers or they are in reagent bottles with burette type dispensers. All necessary glassware is available in the kit to perform the analyses. The colorimeter is secured permanently in the case and contains direct reading (mg/l) scales. The kit has the capacity for testing 19 parameters and has simple, easy to follow instructions in the "Methods Manual" which accompanies the kit. They are:

Alkalinity	Hardness	Oxygen, Dissolved
Carbon Dioxide	Hydrogen Sulfide	pH
Chloride	Iron	Phosphate
Chlorine	Manganese	Silica
Chromate	Nitrate	Sulfate
Copper	Nitrite	Turbidity
Fluoride		

PROCEDURE

Specific parameters of interest in preliminary field investigations were evaluated. These parameters are:

Alkalinity	Hardness	pH
Chloride	Iron	Phosphorus
Copper	Manganese	Sulfate
Dissolved Oxygen	Nitrate	

When the Hach procedure called for the use of the colorimeter with precalibrated scales, known standards were measured prior to analyzing samples. Comparisons were made on natural water samples from a variety of sources by measuring the desired constituent with the Hach Kit and also with the method in use in the TA&I laboratory, called Method A in this evaluation. Either the percent deviation or the average deviation in mg/l was calculated using Method A as the correct value. Ten replicates were measured using the kit for 5 of the parameters. When replicates were measured, the standard deviation (σ) was calculated using the following formula:

$$\sigma = \sqrt{\frac{n(\sum X^2) - (\sum X)^2}{n(n-1)}}$$

X = value in mg/l
n = Number of replicates

RESULTS

The data for comparison of the two methods are in Table 1. The data from the replicates are in Table 2. The results of known standards analyzed using the Hach Kit appear in Table 3 and Figures 1 through 7 respectively.

1. Alkalinity

Method A and the Hach method are titration procedures with standard sulfuric acid. The end-points of pH 4.5 and 8.3 are determined using a pH meter with a glass electrode for Method A. The Hach method utilizes the color change of bromocresol green-methyl red and phenolphthalein as the end-points. The results are recorded in mg/l as CaCO_3 .

The range of alkalinity was 0 to 770 mg/l for the pH 4.5 end-point and 0 - 300 mg/l for the pH 8.3 end-point.

The average percent deviation for the results obtained with the Hach Kit at the end-point of pH 4.5 was 30% and at the end-point of pH 8.3, deviation was 26%.

The 10 replicates had a mean value of 196 mg/l, the high was 200 mg/l and the low 190 mg/l. The standard deviation was 5.2 mg/l.

2. Chloride

Both the Hach method and Method A utilize mercuric nitrate as the titrant and diphenylcarbazone as the indicator. The results are recorded in mg/l chloride. The range of the samples was 15 to 170 mg/l with the exception of two samples that had values greater than 19,000 mg/l. The average percent difference was 4.7%. The 10 replicates had a high value of 62 mg/l and a low of 56 mg/l. The standard deviation was 1.8 mg/l at the mean of 60 mg/l.

3. Copper

Copper was measured colorimetrically using the Hach Kit, with cuprethol as the chelating reagent. Atomic absorption spectrophotometry was used as Method A. Figure 1 is a graph of known standards versus the results obtained with the Hach Kit. It should be noted that the Hach Kit gave high results for each of the standards. The samples used for comparison of procedures contained from 0 to 3.4 mg/l copper. The percent difference is not as meaningful as the actual differences of the comparisons which averaged 0.13 mg/l. Thirteen

values obtained with the Hach Kit showed a positive deviation, 4 showed a negative deviation and 3 showed no difference.

4. Dissolved Oxygen (D.O.)

The modified azide-Winkler method was used for both Method A and the Hach method, the only difference was the titrant. Sodium thiosulfate was used for Method A and phenylarsene oxide for the Hach method. A variation from the Methods Manual was made on this test; instead of the recommended ml. of sample to be titrated, 11.6 ml. was taken. This made each drop of titrant equal to 0.5 mg/l dissolved oxygen.

The range of the D.O. was 4.1 to 13.6 mg/l. The average difference between the two methods was 0.6 mg/l. Two Hach results were low, one showed no deviation and 17 were high.

5. Hardness

Total hardness is reported as mg/l CaCO_3 . Both Method A and the Hach method employ the EDTA titration procedure. The range of total hardness was 14 to 540 mg/l. The average percent difference was 13%, 4 results were low, 13 were high and 3 showed no deviation. The 10 replicates had a standard deviation of 2.8 mg/l at the mean of 88 mg/l. The high value was 95 mg/l and the low value was 80 mg/l.

6. Iron

Atomic absorption spectrophotometry was used as Method A and O-phenanthroline was used for color development for the Hach method.

Three known standards were analyzed with the Hach Kit; these value are shown in Figure 2.

The range of sample concentrations used for comparison of procedures was < 0.1 to 3.0 mg/l. The average difference was 0.13 mg/l, with 11 positive deviations, 3 negative and 6 results exhibited no deviation.

7. Manganese

The "Cold Periodate Oxidation Method" was utilized with the Hach Kit and Atomic Absorption Spectrophotometry was employed as Method A. Seven samples were then analyzed by both methods, the range was from 0.5 to 9.3 mg/l. The Hach method showed extremely poor sensitivity and the average deviation was 3.7 mg/l.

Three known standards were analyzed with the Hach Kit and the values obtained were extremely low (Figure 3).

8. Nitrate

Method A was the modified brucine procedure. The cadmium reduction method was used for the Hach method. The direct reading scale is from 0 to 150 mg/l nitrogen which is present as nitrate; therefore, instead of using a 0.25 ml. sample as suggested by the method manual, a 25 ml. sample was used and the scale divided by 100 . Five known standards were measured with the Hach Kit and the results are in Figure 4. The range of concentrations in samples used for comparison of procedures was from < 0.1 to 3.5 mg/l. The average difference was 0.16 mg/l with 13 high results, 2 low results and 5 results that showed no difference.

9. pH

A pH meter with a glass electrode was used for Method A and the Hach method consists of adding a wide range indicator and measuring the pH colorimetrically. Five standard buffers were measured using the Hach Kit and the results appear in Figure 5. At the lower end of the scale the results were slightly high. The samples used for comparison ranged from pH 1 to 11.7. The wide range indicator is only applicable between pH 4.0 to 10.0, but it was important to check samples out of this range to insure that they would be reported either below or above the applicable range. For those samples which had pH values between 4 and 10, the average deviation was 0.3 units with the exception of one sample which was too turbid to zero on the colorimeter. One sample with pH 3.8, read pH 4.4 by Hach method; all other samples below pH 4.0 or above pH 10.0 were measured out of range by Hach Kit. Ten replicates had a standard deviation of 0.25 pH units at the mean of 8.1 pH units, the range was from 7.8 to 8.4 pH units.

10. Total Phosphate

An automated procedure employing the Technicon Auto Analyzer was used for Method A. The method for both the Hach Kit and the Auto Analyzer was the ammonium molybdate, stannous chloride reduction. All results are recorded as mg/l PO_4 . Five known standards were measured using the Hach Kit and the results are plotted in Figure 6. Four of the five readings were higher than the actual values. The range of concentrations in samples used for comparison had values from < 0.01

to 12.0 mg/l. The Hach Kit scale may be read up to 8 mg/l without dilution, the average difference between the two methods was 0.53 mg/l. The 10 replicates ranged from 4.8 to 5.2 mg/l with a standard deviation of 0.13 mg/l at the mean of 4.9 mg/l.

11. Sulfate

The method for both the Hach Kit and Method A was a turbidimetric procedure with Sulfa Ver powder as the reagent. Three prepared standards were measured using the Hach Kit with the results plotted in Figure 7. The samples used for comparison ranged in sulfate concentration from 14 to 282 mg/l. The average percent difference was 27%. High results were obtained with the Hach Kit on 18 of the 20 samples.

DISCUSSION OF USE

The Hach Kit was found to be sturdy, easy to use, and contained all necessary equipment. The instruction manual is simple and easy to follow. An estimated time to analyze for alkalinity, hardness, iron, D.O., and pH in the field is approximately 30 to 45 minutes. The equipment is of excellent material and the design is extremely compact.

CONCLUSIONS

The design, equipment, reagents and ease of use are all well suited to field use. All of the reagents and equipment are readily available from the Hach Chemical Company.

No quality control system is built in and, therefore, a verification of the results using known standards is a necessity.

The results obtained for this evaluation were made under laboratory conditions and are probably better than those that would be obtained in the field.

With the exception of manganese, all procedures evaluated would be acceptable for showing relative differences in the quality of water. With precalibration, and analyzing known standards, the results would be acceptable for selecting sample points for intensive study.

The results obtained using the Hach Kit would not be acceptable to replace laboratory results except under highly controlled conditions which would, in most cases, negate its utility.

TABLE I. Comparisons of Method A and Hach Method

1. Alkalinity mg/l CaCO_3 pH 8.3			Alkalinity mg/l CaCO_3 pH 4.5			2. Chloride mg/l Cl		
Method A	Hach	% Diff.	Method A	Hach	% Diff.	Method A	Hach	% Diff.
0	0	0	0	0	0	82	72	-12
0	0	0	62	78	+25	22	22	0
0	0	0	140	140	0	90	87	-3.3
0	0	0	200	200	0	120	120	0
0	0	0	120	120	0	170	170	0
0	0	0	170	180	+5.9	130	120	-7.7
0	0	0	200	530	+115	34	38	+12
0	0	0	0	0	0	33	32	-3.0
0	0	0	0	0	0	64	60	-6.2
60	110	+83	230	770	+235	60	59	-1.7
85	53	-38	180	160	-11	20	16	-20
0	0	0	0	0	0	15	15	0
0	0	0	90	94	+4.4	100	100	0
60	74	+23	220	220	0	94	93	-1.1
290	300	+3.4	470	410	-13	60	60	0
0	0	0	0	0	0	58	59	+1.7
130	120	-7.7	300	300	0	60	54	-10
0	0	0	80	86	+7.5	60	56	-6.7
250	240	-4.0	370	360	-2.7	>19,000	17,400	*
0	0	0	100	130	+30	>19,000	17,500	*
	Avg.	26		Avg.	30		Avg.	4.7

*Result outside limits of test.

TABLE I. - Continued

3. Copper mg/l Cu			4. Dissolved Oxygen mg/l mg/l D.O.			5. Hardness mg/l CaCO ₃		
Method A	Hach	Diff. mg/l	Method A	Hach	Diff. mg/l	Method A	Hach	% Diff.
0.7	0.5	-0.2	11.0	12.5	+1.5	400	400	0
0.1	0.1	*	10.8	11.5	+0.7	170	140	-18
0.1	0.1	0	10.7	11.5	+0.8	57	60	+ 5.3
0.6	0.5	-0.1	4.1	4.5	+0.4	280	180	-36
0.9	0.8	-0.1	4.6	5.5	+0.9	190	160	-16
0.9	0.8	-0.1	6.2	7.0	+0.8	170	180	+ 5.9
0.2	0.1	*	6.6	7.0	+0.4	240	250	+ 4.2
2.9	2.6	-0.3	7.1	8.0	+0.9	200	210	+ 5.0
0.4	0.2	-0.4	13.6	13.5	-0.1	540	560	+ 3.7
1.3	1.2	-0.1	13.5	13.5	0	130	130	0
1.0	1.0	0	12.1	11.5	-0.6	71	80	+13
2.4	2.5	+0.1	10.6	11.5	+0.9	430	430	0
0.2	0.1	-0.1	9.4	10.5	+1.1	130	140	+ 7.7
0.2	0.1	*	9.3	10	+0.7	43	50	+16
2.0	2.0	0	7.9	8.5	+0.6	14	20	+43
0.4	0.3	-0.1	6.6	7.0	+0.4	410	440	+ 7.3
2.2	2.3	+0.1	5.1	5.5	+0.4	95	100	+ 5.3
3.0	3.4	+0.4	7.7	8.5	+0.8	29	40	+38
0.9	0.8	-0.1	6.3	6.5	+0.2	83	70	-16
0.2	0.1	*	4.9	5.0	+0.1	130	160	+23
	Avg.	4.7		Avg.	0.6		Avg.	13

6. Iron mg/l Fe			7. Manganese mg/l Mn			8. Nitrate mg/l NO ₃ -N		
Method A	Hach	Diff. mg/l	Method A	Hach	Diff. mg/l	Method A	Hach	Diff. mg/l
1.5	1.8	+0.3	0.5	0.7	+0.2	0.2	0.1	-0.1
2.6	2.7	+0.1	9.9	1.8	-8.1	0.4	0.6	+0.2
3.0	2.9	-0.1	2.5	1.2	-1.3	0.1	0.1	0
0.2	0.4	+0.2	0.5	0.8	+0.3	1.2	1.3	+0.1
1.0	1.0	0	9.3	1.7	-7.5	0.3	1.2	+0.9
<0.1	0.1	*	8.0	1.4	-6.6	0.1	0.5	+0.4
<0.1	0.1	*	3.2	1.0	-2.2	<0.1	0.2	*
2.4	2.2	-0.2		Avg.	3.7	<0.1	0.1	*
1.2	1.4	+0.2				<0.1	0.2	*
0.4	1.0	+0.6				0.5	0.4	-0.1
1.3	1.5	+0.2				0.3	0.3	0
0.9	0.9	0				0.2	0.2	0
0.9	0.8	-0.1				0.4	0.5	+0.1
0.5	0.5	0				0.8	0.9	+0.1
0.3	0.3	0				1.0	1.0	0
0.1	0.1	0				0.8	1.0	+0.2
0.2	0.3	+0.1				1.6	1.7	+0.1
0.9	1.0	+0.1				1.9	1.9	0
0.7	0.7	0				2.9	3.0	+0.1
<0.1	0.1	*				3.5	3.8	+0.3
	Avg.	0.13					Avg.	0.16

TABLE I. - Continued

9. pH			10. Phosphate mg/l PO_4			11. Sulfate mg/l SO_4		
Method A	Hach	Diff.	Method A	Hach	Diff. mg/l	Method A	Hach	% Diff.
0.2	< 4	*	3.8	3.3	-0.5	146	155	+ 6.2
1.2	< 4	*	4.2	3.8	-0.6	155	170	+ 9.7
1.0	< 4	*	2.8	2.6	-0.2	155	155	0
11.7	>10	*	3.1	3.2	+0.1	140	220	+57
9.4	9.2	-0.2	1.8	0.6	-1.2	210	300	+43
7.1	8.2	+1.1	12	>8	*	163	200	+23
4.8	4.7	-0.1	5.2	4.1	-1.1	126	175	+39
8.3	8.4	+0.1	1.2	0.9	-0.3	282	>300	*
7.5	*	*	0.28	0.5	+0.22	249	>300	*
5.5	5.3	-0.2	6.5	5.1	-1.4	14	17	+21
10.5	<10	*	6.9	4.9	-2.0	31	29	- 6.4
7.9	8.3	+0.4	7.5	6.3	-1.2	15	19	+27
10.8	>10	*	0.09	0.2	+0.11	47	58	+23
6.9	7.2	+0.3	0.15	0.1	-0.05	61	77	+26
3.5	< 4	*	0.37	0.3	-0.07	214	270	+26
6.8	7.0	+0.2	<0.01	<0.1	*	201	275	+37
8.2	8.4	+0.2	0.9	0.9	0	7	11	+57
8.6	8.6	0	1.7	1.8	+0.1	85	130	+53
4.6	4.5	-0.1	0.25	0.4	+0.15	81	100	+23
3.8	4.4	*	1.4	1.2	-0.2	85	122	+44
	Avg.	0.3		Avg.	0.53		Avg.	27

Table 2 - Replicate Analyses by Hach Method

Alkalinity mg/l CaCO_3	Chloride mg/l Cl	Hardness mg/l CaCO_3	pH	Phosphate mg/l PO_4
200	62	90	7.8	4.8
190	62	85	7.8	5.0
200	60	85	7.8	4.8
190	58	90	8.1	5.0
200	60	85	8.1	4.9
200	60	95	8.2	4.9
200	60	80	8.4	4.8
190	56	90	8.3	5.1
190	59	90	8.3	5.2
200	58	85	8.4	4.9
$\bar{X}$ - 196	$\bar{X}$ - 60	$\bar{X}$ - 88	$\bar{X}$ - 8.1	$\bar{X}$ - 4.9
Max-200	Max-62	Max-95	Max-8.4	Max-5.2
Min-190	Min-56	Min-80	Min-7.8	Min-4.8
σ - 5.2	σ - 1.8	σ - 4.2	σ - 0.24	σ - 0.13

Table 3 - Standards Measured by Hach Method

Copper mg/l Cu		Iron mg/l Fe		Manganese mg/l Mn		Nitrate mg/l NO ₃ -N	
Std.	Hach	Std.	Hach	Std.	Hach	Std.	Hach
0.6	0.7	0.5	0.6	3.0	1.2	0.1	0.1
1.5	1.6	1.0	1.0	5.0	1.1	0.3	0.4
2.0	2.3	2.0	2.1	10.0	1.8	0.6	0.7
6.0	6.4					1.0	1.1
						1.3	1.5

pH		Phosphate mg/l PO ₄		Sulfate mg/l SO ₄	
Std.	Hach	Std.	Hach	Std.	Hach
4.0	<4	1.0	1.4	96	93
4.6	4.5	2.0	2.3	192	185
7.0	7.3	4.0	4.4	288	300
8.0	8.4	6.0	6.2		
9.0	9.1	8.0	7.9		

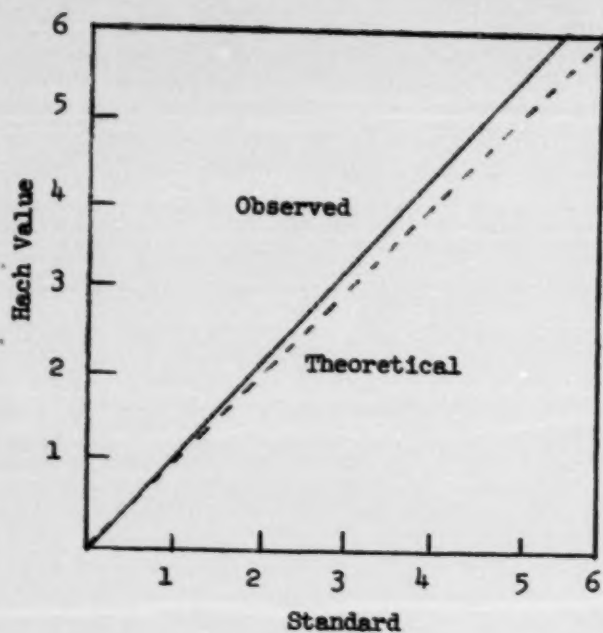


FIGURE 1 - Copper mg/l

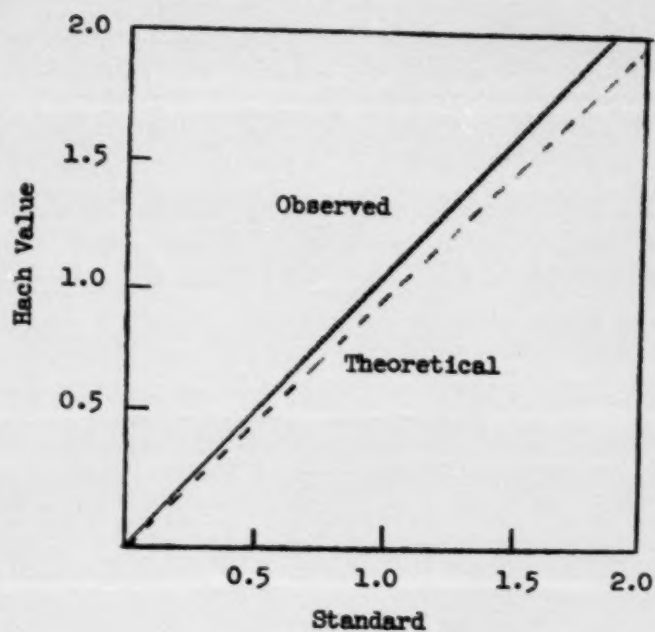


FIGURE 2 - Iron mg/l

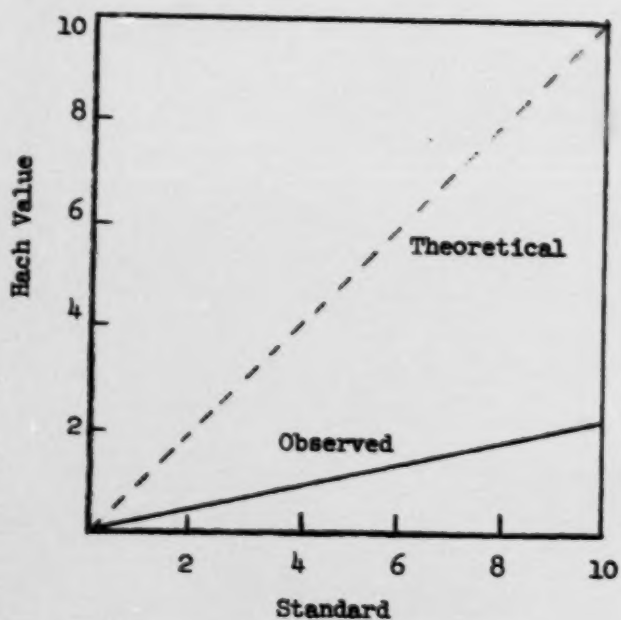


FIGURE 3 - Manganese mg/l

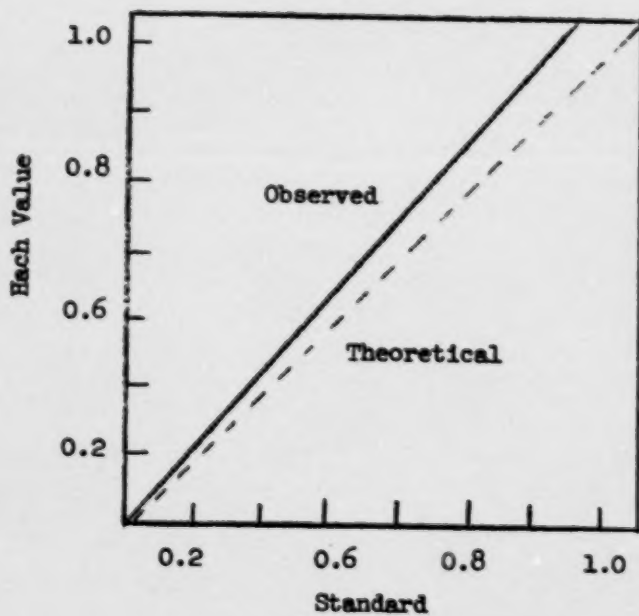


FIGURE 4 - Nitrate mg/l

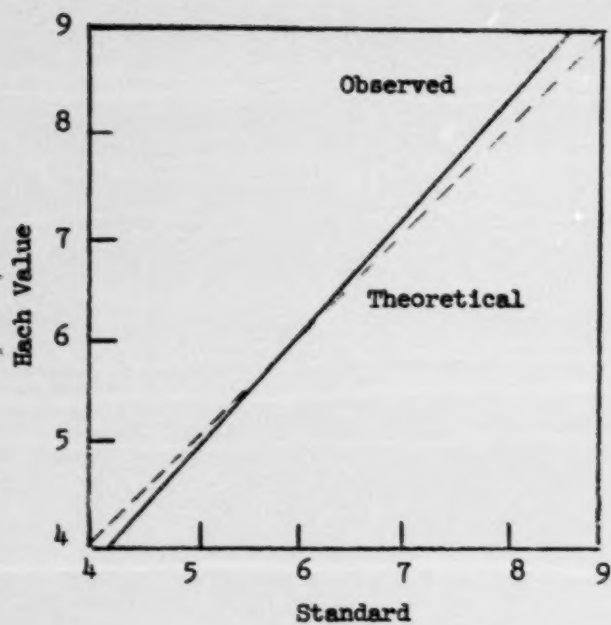


FIGURE 5 - pH Units

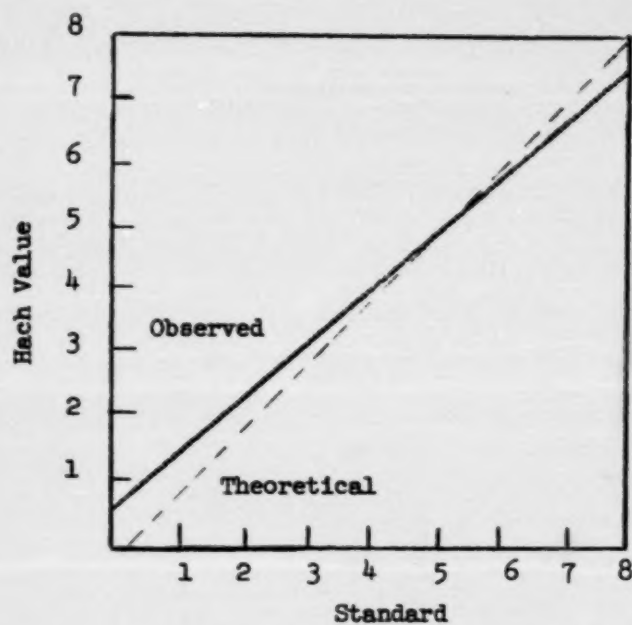


FIGURE 6 - Phosphate mg/l

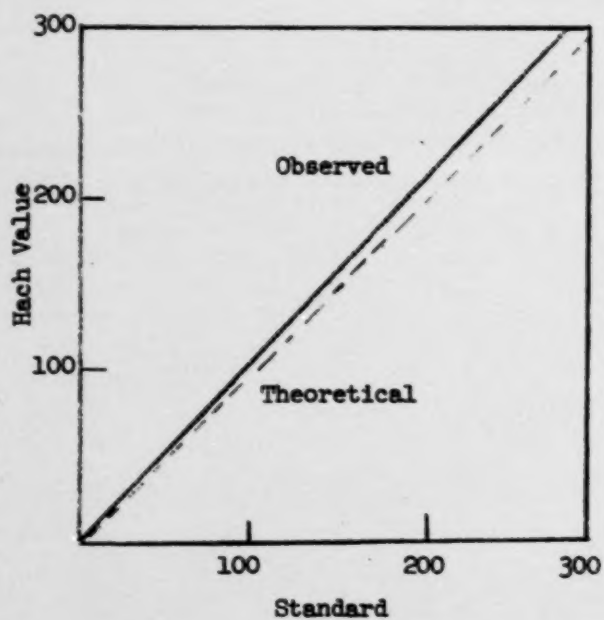


FIGURE 7 - Sulfate mg/l